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IN ONE DIMENSION

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ELECTRON-ELECTRON INTERACTIONS AND BROKEN SYMMETRY
IN ONE DIMENSION

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ABSTRACT

A novel real space approach to dimerization in a half-filled band
is developed to investigate effects of electron-electron interactions
on the Peierls instability. Dimerization is shown to be a result of
imperfect resonance between pairs of electron configurations related
to each other by a mirror plane symmetry passing through the longest
diagonal of the infinite polygon. Coulomb interactions enhance the
barrier to perfect resonance, so that dimerization itself is enhanced
for moderate values of the correlation parameter. Recent experimental
findings and the present theoretical work then suggest that explicit
inclusion of Coulomb interactions between electrons may be necessary
for an accurate description of ground and excited states in poly-
acetylene.

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Current theories of polyacetylene[1-4] usually start from the Hückel limit of zero electron correlation with an electron-phonon coupling constant modulating the nearest neighbor transfer integral. The infinite polyene with a half-filled band of π-electrons is assumed to have a Peierls-dimerized ground state and an optical gap due entirely to dimerization. In spite of the immense success of the above one-electron model in interpreting various experiments in polyacetylene,[5] several questions regarding the role of electron-electron interaction in this material remain unanswered. Thus an alternate origin for the optical gap was proposed many years ago by Ovchinnikov and coworkers;[6] electron-electron repulsion was postulated to be the principal source of the optical gap, and the ground state of the infinite polyene was predicted to have a uniform structure. While recent x-ray[7] and nmr[8] measurements have definitively demonstrated bond-alternation in polyacetylene, considerable evidence of the importance of electron correlations exist. In contradiction to the predictions of one electron theory, the lowest excited state in finite polyenes has been shown to be a ^1A_g state rather than the optical ^1B_u state.[9] Similarly, the occurrence of negative spin densities in finite polyene radicals[10] and polyacetylene[11] underscore the importance of electron correlation. We therefore reexamine here one of the arguments for weak electron correlation in polyacetylene, and demonstrate that the above is based on erroneous theoretical results. Previous discussions of our investigation may be found in Ref. 12 and 13.

The principal argument for weak electron correlation in polyacetylene is based on earlier theoretical work that predict destruction of dimerization in the presence of moderate to strong electron-

electron interaction.[6,14-16] The above investigations are mostly based
on the Hartree-Fock approximation, and we have recently shown that this
approximation is inappropriate for correlated bands.[12,13] Electron-
electron interactions can in fact strongly enhance the dimerization, so
that dimerization by itself is not a suitable criterion for deciding the
role and magnitude of Coulomb interactions.[12,13] In the present paper,
we review our arguments for this enhancement effect. We develop a novel
real space approach to dimerization that is valid for all values of the
correlation parameters, and we show how within our picture the various
effects of Coulomb interactions can be predicted from simple physical
arguments alone. These conclusions are then substantiated by exact
numerical calculations on finite rings, and finite size effects are
shown to be small.

We consider only the π-electrons in polyacetylene and assume
that the adiabatic approximation is valid. The Hamiltonian we con-
sider may then be written in units of t_o, the transfer integral for
the uniform chain, as

$$H/t_o = (U/t_o) \sum_i n_{i\uparrow} n_{i\downarrow} + \sum_{i,\sigma} (1 \pm 2\alpha x)(a_{i\sigma}^+ a_{i+1,\sigma} + h.c.) + 2NKx^2 \quad (1)$$

where x is the displacement of each atom, αt_o the electron-phonon
coupling constant, Kt_o the spring constant, and the N the number of
sites. We consider only the on-site repulsion U. The effects of
intersite Coulomb interactions may be found in Ref. 13.

A simple description of the two degenerate phases in the dimerized state is the double-well potential, in which the system residing at either of the two minima is dimerized, while the system lying at the maximum is uniform. The energy barrier between the two minima is a direct measure of the extent of dimerization, and determination of Coulomb effects on the dimerization then requires knowledge about the Coulomb contribution to this barrier. Since dimerization implies a loss of the mirror-plane symmetry σ_v along the longest diagonal of the infinite polygon (i.e. passing through an atom), the many-electron basis functions dominating the ground state wave function of the dimerized system should themselves be of reduced symmetry. It should therefore be possible to assign "left" and "right" characters to these basis functions, and the Coulomb contribution to the barrier height in the double well potential may then be determined from the effects of the Coulomb term on the barrier to resonance between the two kinds of basis functions. This is discussed below in greater detail, where we develop a valence bond (VB) approach to dimerization in a correlated half-filled band.

Within the VB approach the ground and excited state wave functions are described as linear combinations of VB diagrams, which are them-selves linear combinations of many-electron configurations.[17] Finite segments of a few representative diagrams for the infinite chain are shown in Fig. 1. Here each cross (X) represents a doubly occupied site, a dot ($\cdot$) an empty site, and pairs of singlet-coupled singly occupied sites are represented by a bond. Thus in Fig. 1,

$$|I\rangle = (1/\sqrt{2})^{N/2}(a_{1\alpha}^+a_{2\beta}^+ - a_{1\beta}^+a_{2\alpha}^+)(a_{3\alpha}^+a_{4\beta}^- - a_{3\beta}^+a_{4\alpha}^+) \ldots |0\rangle \qquad (2a)$$

$$\text{and } |VI\rangle = a_{1\alpha}^+a_{1\beta}^+a_{3\alpha}^+a_{3\beta}^+a_{5\alpha}^+a_{5\beta}^+ \ldots |0\rangle \qquad (2b)$$

where $|0\rangle$ is the vacuum. The complete set of diagrams may thus be constructed for arbitrary N by similarly joining all singly occupied sites in all possible manner, with one restriction: only nested (i.e. noncrossing) bonds are allowed.[17] Diagrams with $N_x=0$ will be called covalent, while diagrams with $N_x>0$ will be called ionic, where N_x is the number of doubly occupied sites and varies from 0 to N/2. Nearest neighbors need not have opposite spins, so that long nonnearest bonds are required for a complete description.[17] The two covalent diagrams with only nearest neighbor bonds ($|I\rangle$ and $|II\rangle$ in Fig. 1) will be called Kekulé diagrams while covalent diagrams with at least one bond between nonnearest neighbors will be called Dewar diagrams. All diagrams are diagonal in U, but off-diagonal in H_t, the hopping term in (1).

Notice that $|I\rangle$ and $|II\rangle$ are related by σ_v, and thus favor one kind of dimerized state or another. The diagram $|VI\rangle$ on the other hand, is symmetric with respect to σ_v, and thus favors the uniform structure. All diagrams for an arbitrarily large system may be similarly classified into those favoring dimerization and those favoring the uniform structure. The uniform structure requires exactly equal contributions to the ground state wave function by $|I\rangle$ and $|II\rangle$, and all other pairs related by σ_v. For the correlation problem, we have to consider the resonance between the pair

that favor the dimerization most strongly. The reason for this is easily understood. Equal contributions by any intermediate pair does not necessarily imply equal contributions by the extreme pair, while the converse is always true.

To determine which particular pair of VB diagrams favor the dimerization most strongly we use the definition of the bond order $P_{i,i+1}$ between sites i and i+1,

$$P_{i,i+1} = \frac{1}{2} < \sum_{\sigma} a^+_{i\sigma}a_{i+1\sigma} + a^+_{i+1\sigma}a_{i\sigma} > \tag{3}$$

Consider now a sequence of three sites i-1, i and i+1. If site i is singly occupied the largest difference between $P_{i,i+1}$ and $P_{i-1,i}$ occurs when both i+1 and i-1 are singly occupied, but one of them is occupied by an electron with the same spin as the one occupying i, while the other is occupied by an electron with opposite spin. Similarly if i is doubly occupied, the largest difference between $P_{i,i+1}$ and $P_{i-1,i}$ occurs when one of the sites i±1 is also doubly occupied while the other is empty. VB diagrams which favor the dimerization most strongly must have one of these local arrangements repeated throughout the length of the chain. The former arrangement is repeated only in the two Kekulé diagrams |I> and |II>, as all bonded sites necessarily have opposite spins, while nearest neighbor nonbonded sites have parallel and opposite spins with equal probability. The second local arrangement has the repeat unit 2200, where the numbers 2 and 0 signify doubly occupied and vacant sites. Since we are interested only in 4n+2-electron rings,[13] where n is an integer, it is easily seen that this latter arrangement cannot

be maintained throughout the length of the ring. In a 4n+2-electron ring then dimerization is most strongly favored by the two Kekulé diagrams.[13]

We therefore consider the barrier to resonance between the two diagrams $|I>$ and $|II>$. We start from $|I>$ and apply H_t repeatedly until we reach $|II>$. The initial step requires creation of a double occupancy and a hole, but after this at each step bifurcations are possible: the double occupancy or the hole can move to the left or right, or a new pair of double occupancy and hole may be created (destroyed). Such bifurcations lead to many possible paths between $|I>$ and $|II>$, each characterized by the largest N_x involved. Rep-resentative paths for the N=6 case are shown in Fig. 2, and it should be obvious that similar paths may be constructed for arbitrary N. The important point is that the minimum length of these paths is always N, the system size. Since only H_t connects two consecutive diagrams along any path, the length of the paths is a direct measure of the kinetic energy contribution to the barrier to resonance between $|I>$ and $|II>$. At U=0 all paths are equally probable, and for an infinite system, paths are sufficiently long to give a dimerized state, in which the contribution of $|I>$ and $|II>$ (and all other pairs symmetrically related to these) are unequal. For U>0, there is an additional potential energy contribution $\sim N_x U$ to the barrier along each path. The barrier to resonance thus rises considerably, and dimerization is enhanced compared to the U=0 case.

Since all $P_{i,i+1}$ go to zero, however, at $U = \infty$, a reversal in the enhancement effect is expected at a certain U_{rev}. This reversal is

due to virtual transfers between neighboring nonbonded sites. Virtual transfers involve double hops in which an electron at site i hops to i+1 and creates a double occupancy, and then one of the two electrons at i+1 hops back to i. If the electron at i now is the one originally occupying i+1, bonding patterns are severly affected. Thus virtural transfers between sites 2 and 3 in |I> in Fig. 1 lead to the Dewar diagram |V>. Paths involving virtual transfers and covalent diagrams only may therefore be constructed betw en |I> and |II>, and these paths are considerably shorter. The lengths of these paths is only (N/2-1), so that the barrier to resonance is considerably lower once virtual transfers dominate over real transfers. The requirement for this is that the net contribution of covalent diagrams to the ground state wave-function, starting from an asymptotic value of zero at U=0, is larger than the contributions of all ionic diagrams.

The minimum magnitude of U at which the covalent diagrams dominate may be obtained from the exact expression for the optical gap in the undimerized Hubbard chain. The optical gap, which is the minimum energy of a real transfer, if $\sim U-4t_o$ in the large U limit. For $U \rightarrow \infty$ the ground state consists of covalent diagrams only and the minimum value of U at which the covalent diagrams dominate then is the smallest U at which the large U expression for the optical gap is valid, viz, $U \sim 4t_o$. Thus for $0 \leqslant U \leqslant 4t_o$, the tendency to dimerization is progressively enhanced, while from $U \sim 4t_o$ onward dimerization decreases smoothly.

We have performed exact numerical calculations for the finite rings N=6 and N=10 to verify the above conclusions. Finite systems

exhibit dimerization only for α greater than N-dependent threshold values. However, the effect of U is local and the behavior of such finite systems near the threshold α should mimic the behavior of the infinite system near $\alpha \to 0+$. For each N then, we choose the smallest K/α^2 for which the system is barely undimerized at U=0 and calculate the total energy $E(U,\alpha x)$, electronic plus elastic, and the stabilization energy gained per electron on dimerization,

$$\frac{\Delta E}{Nt_o} = \frac{1}{Nt_o} \{E(U,\alpha x) - E(U,0)\} \tag{4}$$

In Figs. 3(a) and (b) we present our results for N=6 and 10 respectively. The strong enhancement for $U/\sqrt{2} \, t_o \lesssim 3$ and the smooth decrease in the enhancement factor beyond this is obvious in both cases. Fnite size effects can be expected to be small since the ground state energy density is known to converge much faster than excitations. Convergence here may be checked most easily by comparing the energy densities of the N=6 and N=10 rings with those of the infinite system for the two cases, (i) U=0, $\alpha x \neq 0$, and (ii) $U \neq 0$, $\alpha x = 0$. In both cases the N=10 results are closer to those for the infinite system than to those for N=6, and are virtually identical[13] with the former for $\alpha x \gtrsim 0.1$ and $U \gtrsim 4t_o$. We have also examined the exact undimerized wavefunctions in detail as a function of U/t_o. These results indicate[13] that the covalent diagrams dominate the ground state wave-function only from $U \sim 4t_o$ onwards, as predicted, thus further verifying that $U_{reV} \sim 4t_o$.

We have also investigated the effects of various intersite Coulomb interactions in detail. As with the on-site term, the effect of each

individual intersite interaction can be predicted from their effect on the barrier to resonance.[13] These interactions further enhance the dimerization greatly, except in the case where all interactions beyond the nearest neighbor are zero and the nearest neighbor interaction is greater than 1/2 U.

To summarize then, previous theoretical results concerning the dimerization in a correlated half-filled band are mostly erroneous. Dimerization in polyacetylene does not imply $U < 2t_o$, nor is it possible to define an effective electron-phonon coupling constant for the highly correlated band that results for $U > 2t_o$. Accurate estimates of the various parameters in (1) are therefore required for a more correct description of polyacetylene. The effect of the correlation terms on the soliton and polaron-like excitations in this system are currently being investigated.

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FIGURE CAPTIONS

Fig. 1.   Finite segments of representative VB diagrams (see text) for
a half-filled band. The site indices have been included at the
top and the bottom.

Fig. 2.   Representative paths in configuration space connecting the two
Kekulé diagrams in N=6. Pairs of consecutive diagrams are
related by the hopping term H_t in Eq. (1). Similar paths may
be constructed for arbitrarily large N.

Fig. 3.   Energy gained per electron on dimerization for the six and ten
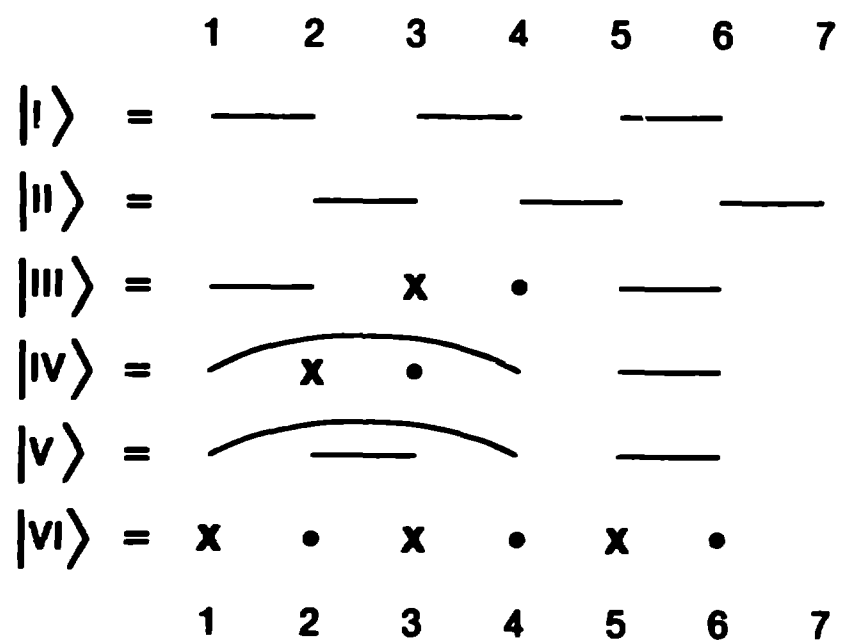membered rings. The numbers against each curve are the different
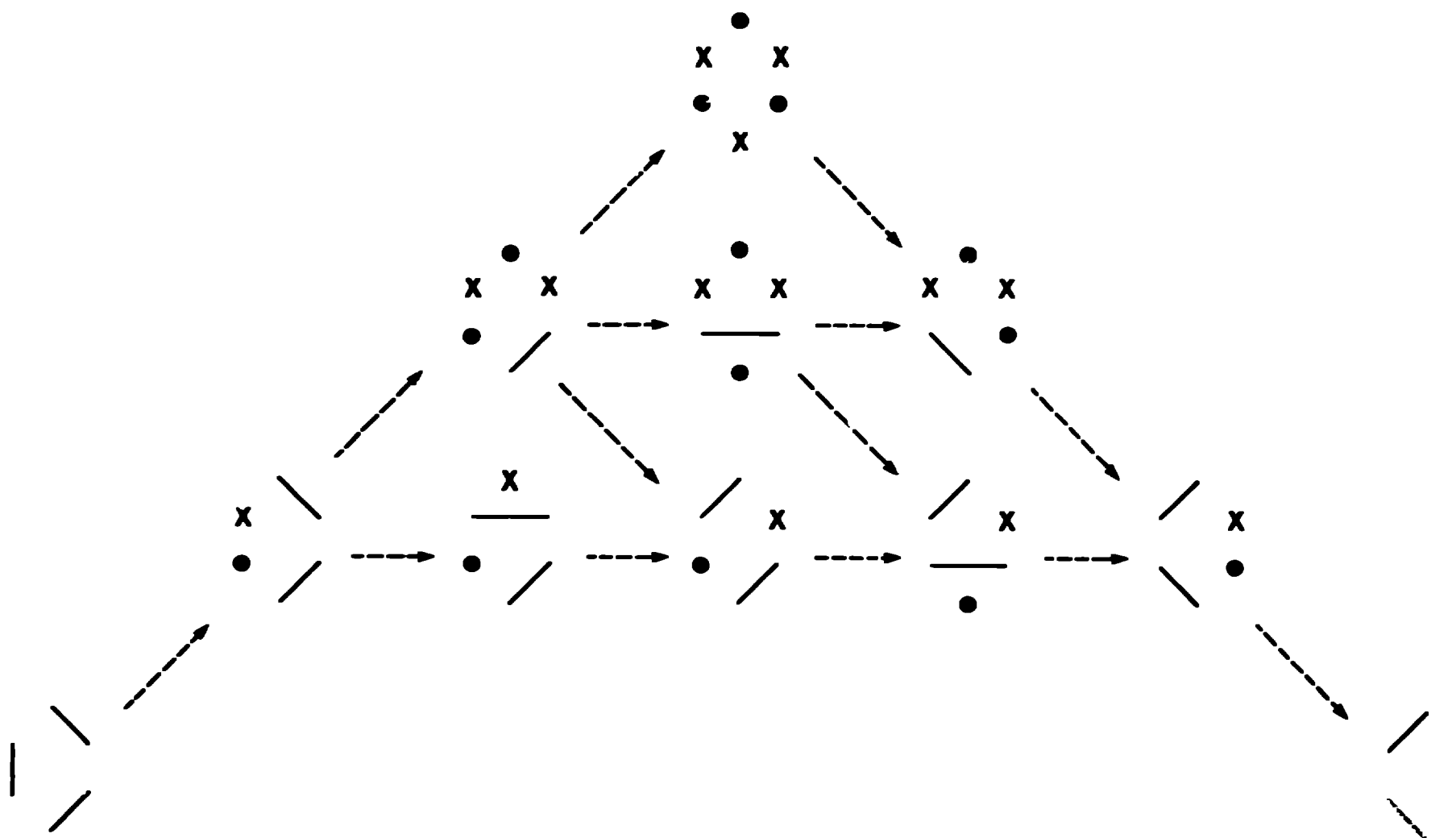values of $U/\sqrt{2}\, t_o$.

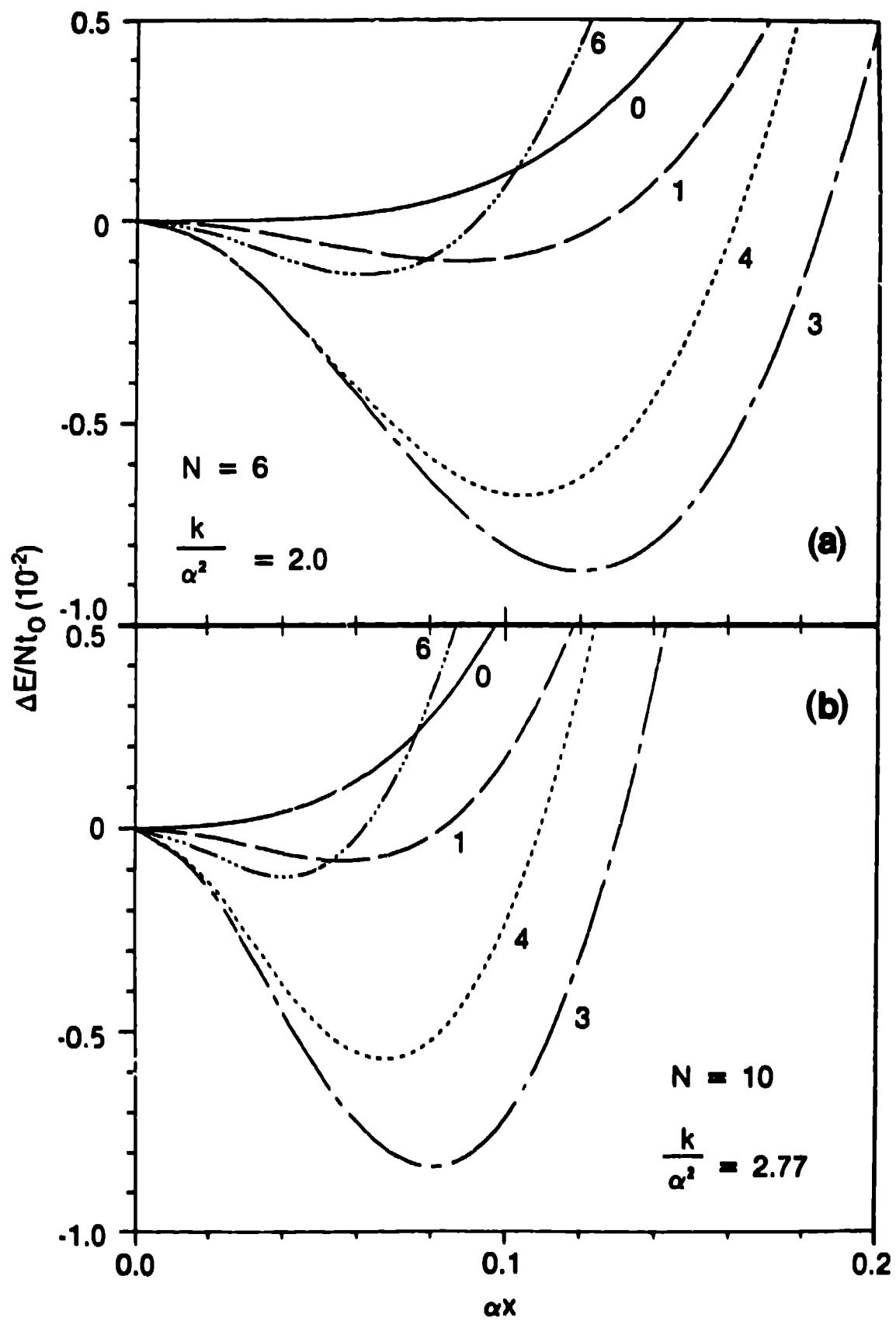Fig. 1. Mazumdar and Dixit

Fig. 2, Mazumdar and Dixit

Fig. 3. Mazumdar and Dixit